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(54) Title: PROCESS OF MAKING SURFACE SIZED PAPER PRODUCTS AND SURFACE SIZING COMPOSITION FOR USE THEREIN

(57) Abstract

A process of making surface sized paper products, in which an aqueous, starch containing surface sizing composition is employed, and a corresponding aqueous, starch containing surface sizing composition are described. Besides starch at least one water soluble polymer and at least one water insoluble polymer are employed. Surprisingly a surface sizing is achieved by this combination which avoids the disadvantages of the use of a water soluble or a water insoluble polymer alone, but at the same time maintains the benefits of the use of water soluble or water insoluble polymer alone.

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Process of making surface sized paper products and surface sizing composition for use therein

The present invention relates to a process of making surface sized paper products by applying to the surface an aqueous, starch containing surface sizing composition followed by drying. Further, the invention relates to an aqueous, starch containing surface sizing composition.

Multiple-purpose printing paper (inkjet, copy, writing) is surface sized for quality improvement, in particular printability. This is generally done by applying an aqueous blend of starch, optical brightener (optional), salt and a polymer to the paper. The polymer is added in order to improve the film-forming properties of the surface size.

Two different types of polymers can be used, namely water insoluble, water dispersible polymers and water soluble polymers. Both have their distinct benefits and drawbacks.

Water soluble polymers typically provide the following advantages: high friction, improved optical density of the inks,

reduced bleeding, wicking, strike through. Disadvantages of water soluble polymers are: extensive foam formation, reduced waterfastness.

Water insoluble polymers typically have the following advantages: no foam formation of the surface size itself, improved film properties (more elastic, water resistant), good waterfastness, improved optical density of the inks, reduced bleeding, wicking, strike through. One disadvantage of water insoluble polymers is: low friction (reducing mechanical sheet control during printing). Another disadavantage of the hydrophobic water insoluble polymers is that they are not compatible with the hydrophilic starch, unless special additives are used as compatibilizers. The result is that the sheet behaves as if it was covered with starch only and the printability is not improved that much.

It is believed that the non-compatible water insoluble polymer is only loosely connected with the starch film covering the paper sheet. Upon rewetting (e.g. during printing) the polymer is easily separated from the starch. In contrast, the polymer that is compatible with the solid film is "anchored" in the starch. Upon rewetting the polymer remains attached to the starch resulting in hydrophobic micro patches.

A known method for compatibilizing water insoluble polymers consists of the addition of cationic starch during the synthesis of the water insoluble polymer by emulsion copolymerisation at high temperature (see DE 43 38 486 A1). Further it is known from PCT application WO 96/09345 and corresponding US patents 5 362 573, 5 460 645 and 5 472 485 to improve surface sizing by adding to the starch containing aqueous surface sizing composition an alkali salt of a Group IV metal (e.g. zirconium, hafnium and titanium).

The importance of compatability is demonstrated by comparative Cobb measurements after surface sizing with different surface

sizes. Typical results of such measurements are summarized in the following table.

Surface sizing with	$Cobb^{60}$ (g/m^2)
starch	55
polymer 1 (not compatible)	20
polymer 2 (compatible)	20
starch + polymer 1	50
starch + polymer 2	20

As can be seen from the above table the sheet surface sized with a combination of starch and non-compatible polymer 1 behaves if it was only covered with starch, i.e. there is only a minor improvement. In contrast the sheet surfaced sized with a combination of starch and compatible polymer 2 behaves more hydrophobically than in the case of starch combined with incompatible polymer. Cobb = 30 would indicate sufficient compatability with the starch so that good printability is obtained.

In the afore-mentioned references the requirements to be met by high printing and writing grade paper products and the advantages provided by surface sizing as well as the manner in which surface sizing is accomplished are described in detail. Insofar the disclosure of these publications is included herein by reference.

It has now been surprisingly found that surface sizing of paper products can be facilitated and/or improved by using an aqueous surface sizing composition comprising besides starch a water insoluble polymer and a water soluble polymer.

Thus the present inventon relates to a process of making surface sized paper products by applying to the surface an aqueous, starch containing surface sizing composition followed by drying, characterized in that said aqueous surface sizing composition further comprises a) at least one water soluble polymer and b) at least one water insoluble polymer.

Further the invention relates to an aqueous, starch containing surface sizing composition for use in a process of making surface sized paper products, said composition further comprising at least one water soluble polymer and at least one water insoluble polymer.

Preferred embodiments of the present invention will become apparent from the following description and the claims. The term "polymer" is used herein in its broad meaning and also covers copolymers obtained by polymerizing two or more monomers.

The paper products useful for surface sizing according to the invention can be any paper or cardboard obtained from known raw materials. Preferably the paper or cardboard is internally sized. Internal sizing can be achieved with any of the known internal sizing agents (reference is made to the above discussed prior art and particularly DE 43 38 486 A1, page 2, lines 50 to 64). Preferred internal sizing agents are alkylketene dimers (AKD), alkenyl succinic anhydrides (ASA) and rosins (preferably fortified rosins). Furthermore the present invention is particularly advantageous with paper products containing fillers like calcium carbonate and the like (see again DE 43 38 486 A1, page 2, lines 54 to 58).

The starch useful in the present invention can be any starch like natural, degraded, converted or chemically modified starches (see again the above cited prior art references). Preferred are cationic starches.

The water soluble polymers useful in the present invention are well known and many of them are marketed as surface sizing polymers.

Particularly useful are polymers obtained by using one or more of styrene, acrylate and methacrylate. Preferably copolymers of styrene and comonomers like acrylic acid and maleic acid or maleic anhydride (SMA) are used. These copolymers are commercially available or can be readily prepared according to known methods.

Another group of water soluble polymers useful in the present invention are polyacrylamides, in particular cationic polyacrylamides (cPAM). Again these polymers are commercially available or can be readily prepared according to known methods.

Further useful water soluble polymers are polyvinyl alcohols, polyvinyl pyrrolidones, polyamido amides, polyethylene imines and polyvinyl amines, all of which are commercially available or readily obtainable by known methods.

The water insoluble polymers useful in the present invention are water dispersible and are also known for surface sizing (see again DE 43 38 486 A1). Particularly useful are polymers obtained by using styrene or butylacrylate or both. Preferred are copolymers of styrene and/or butylacrylate with acrylic acid or butadiene (e.g. a copolymer obtained from a monomer blend comprising 42 mol % of styrene, 28 mol % of butylacrylate and 30 mol % of acrylic acid). Again these polymers are commercially available or can be readily prepared by known methods. Generally speaking they are obtained by emulsion polymerisation in form of latices wherein the inside of the particles consists mainly of the hydrophobic monomers (styrene, butylacrylate) and the outside of the particles consists mainly of the hydrophilic monomers (e.g. acrylic acid), forming "hairy tails" stabilizing the hydrophobic particles. Depending on the desired properties of the

final paper products these water insoluble polymers are selected with regard to glass-transition temperature, minimum film-forming temperature and acrylic acid content.

The aqueous surface sizing composition comprises conventional amounts of starch, e.g. 10 to 200 g/l, preferably about 15 to 50 g/l.

The water soluble and water insoluble polymers are used in a weight ratio of 2 - 50% to 98 - 50%, preferably 3 - 25% to 97 - 75%, and particularly preferred 5 - 10% to 95 - 90% (e.g. 7 - 8% to 93 - 92%). The total amount of water soluble and water insoluble polymers can vary but usually is in the range of 2 - 25% by weight, based on the starch, preferably 5 - 20% by weight, and particularly preferred 10 - 15% by weight (e.g. 12 - 13% by weight).

The total solids content or active content of the aqueous surface sizing composition is also within the usual ranges (see the above cited prior art references). Preferably the surface sizing composition comprises 1 - 20% by weight and particularly preferred 2 - 10% by weight of active ingredients.

Unless otherwise indicated all weights, weight ratios and weight percentages are based on the solids content, i.e. these values relate to the solid contents of the aqueous solutions or dispersions generally used when practising the present invention.

The aqueous surface sizing composition according to the present invention is applied to the surface of the paper product in the normal manner e.g. by a size applicator, preferably during the paper making process (see again the above cited prior art references). For optimum sizing suitable amounts can be determined by tests. In general the uptake of service sizing composition is in the range of 5 to 50 kg (solids) per ton paper, corresponding to 0.5 to 5% by weight (solids) based on the weight of the pa-

per. However, in many cases very good results are already obtained with relatively low amounts in the range of 0.5 to 1.5 % by weight.

The present invention provides a new way for blending (advantageously cold blending) of surface size water soluble and water insoluble polymers resulting in a synergistic improvement of the quality of the paper products, particularly print quality. It is believed that the water soluble polymer functions as a compatibilizer for the water insoluble polymer. The polymer blend performs better than either one of the pure polymers on its own. All benefits of both species are maintained and the drawbacks are covered. The resulting paper product shows no foam, high friction, improved film properties (elasticity, water resistance), good waterfastness, improved optical density of the inks, reduced bleeding, wicking and strike through. For example when using starch together with water soluble polymer as well as water insoluble polymer in the above discussed comparative Cobb measurements typically $Cobb^{60}$ values of about 20 are obtained, indicating that the water insoluble, incompatible polymer is indeed anchored in the starch and thus takes part in the formation of hydrophobic micro patches on the surface of the paper sheet.

Optionally additional components for improving surface sizing can be employed. Useful are for example the Group IV metal salts disclosed in PCT application WO 96/09345 and corresponding US patents 5 362 573, 5 460 645 and 5 472 485, the disclosure of which is herewith included by reference. A preferred salt is ammonium zirconium carbonate (AZC). Such additional components are generally added in an amount of 0.05 - 5% by weight and preferably 0.1 - 2.5% by weight (e.g. 1,4 - 2,0% by weight), based on the combined weight of starch and water soluble and water insoluble polymers.

As stated above the aqueous surface sizing composition usually also comprises optical brightener and salt like alkali salts, e.g. sodium chloride. Furthermore it can include auxiliary materials like defoamers, bactericides, pigments, alkali, and the like as required (compare again the above cited prior art references).

Example

Commercial AKD sized sheets were surface sized in a Mathis Size Press. The surface sizing mixture was 5% active and contained starch (Perlsize K98L sold by Lyckeby Staerkelsen), polymer, optical brightener (Tinopal ABP from Ciba), sodium chloride. The relative ratio by weight was 44/6/3/1.5 for starch/polymer/optical brightner/salt in the surface size mixture. In this context it has to be noted that the term "polymer" includes all solid ingredients of the below defined dispersions, solutions and blends. The sheets were dried in a Schroeter sheet dryer and subsequently test-printed on a HP Inkjet 500C. The print quality was evaluated using a MacBeth colour densitometer. The Hewlett Packard test was used to measure optical density of the composite black colour and the waterfastness of the black ink.

Products used to surface size sheets	Starch + polymer Cobb^{60} (g/m2)	Black intensity L ΔL(CIELab) min. = best	Foam reduction + + + + = best	Waterfastness (L): min. = best
blank 1: not surface sized sheet	43	0	0	
blank 2: surface sized with starch	55	-0.70	+	9.0
disp1	54	-1.40	+ + + +	7.8
solu1	19	-0.3	0	9.5
blend1 (invention)	30	-1.30	+ +	8.5
blend2 (invention)	32	-1.59	+ + + +	5.4
blend3 (invention)	41	-1.17	+ + +	6.2
blend4 (invention)	24	-0.97	+ + +	7.1
blend5	34	-1.17	+ + +	8.8
blend6	28	-040	0	9.3

disp1	=	Water insoluble, emulsion polymerized, random copolymer Styrene/Butylacrylate/acrylic acid (25% active)
disp2	=	Water insoluble, emulsion polymerized, random copolymer Styrene/Butadiene (50% active)
solu1	=	Water soluble ammonium salt of solution polymerized Styrene/acrylic acid copolymer (20% active)
compo	=	Ammonium zirconium carbonate (50% active)
solu2	=	Water soluble cationic polyacrylamide (13% active; 2 000 000 g/mol Mw)
blend1	=	93.3% disp1 + 6,7% solu1
blend2	=	86% disp1 + 8% solu1 + 6% compo
blend3	=	72.8% disp1 + 6.7% solu1 + 2.3% solu2 + 18.2% water
blend4	=	60% disp2 + 8% solu1 + 6% compo + 26% water
blend5	=	98% disp1 + 2% compo
blend6	=	81.8% solu1 + 18.2% compo

Discussion:

The above reported results clearly demonstrate the trend that a better overall performance is observed when using the blends according to the present invention in comparison to disp1 and solu1. Neither blend 5 nor blend 6 gives the same good performance, which demonstrates that the good performance is not attributed to the use of zirconium salt alone.

Claims

1. A process of making surface sized paper products by applying to the surface an aqueous, starch containing surface sizing composition followed by drying, characterized in that said aqueous surface sizing composition further comprises
   a) at least one water soluble polymer and
   b) at least one water insoluble polymer.

2. Process according to claim 1 in which the at least one water soluble polymer (a) comprises at least one polymer selected from the group consisting of polymers containing one or more of styrene, acrylate and methacrylate, cationic polyacrylamides and mixtures therof.

3. Process according to claim 1 or 2 in which the at least one water insoluble polymer (b) comprises a polymer containing styrene or butylacrylate or both.

4. Process according to any of claims 1 to 3 in which the at least one water soluble polymer (a) comprises a styrene/acrylate copolymer.

5. Process according to any of claims 1 to 4 in which the at least one water insoluble polymer (b) comprises a styrene/butylacrylate/acrylate copolymer or a copolymer containing styrene and butadiene.

6. Process according to any of claims 1 to 5 in which the weight ratio of water soluble polymer (a) to water insoluble polymer (b) is 2 - 50% to 98 - 50% and preferably 3 - 25% to 97 - 75%.

7. Process according to any of claims 1 to 6 in which the combined amount of water soluble polymer (a) and water insoluble polymer (b) is 2 to 25% by weight and preferably 5 to 20% by weight, based on the weight of the starch.

8. Process according to any of claims 1 to 7 in which an additional component selected from Group IV metal salts is added.

9. Process according to any of claims 1 to 8 in which the paper product to be surface sized is an internally sized paper product.

10. Aqueous, starch containing surface sizing composition for use in a process of making surface sized paper products, said composition further comprising
    a) at least one water soluble polymer and
    b) at least one water insoluble polymer.

11. Composition according to claim 10 in which the at least one water soluble polymer (a) comprises at least one polymer selected from the group consisting of polymers containing one or more of styrene, acrylate and methacrylate, cationic polyacrylamides and mixtures thereof.

12. Composition according to claim 10 or 11 in which the the at least one water insoluble polymer (b) comprises a polymer containing styrene or butylacrylate or both.

13. Composition according to any of claims 10 to 12 in which the at least one water soluble polymer (a) comprises a styrene/ acrylate copolymer.

14. Composition according to any of claims 10 to 13 in which the at least one water insoluble polymer (b) comprises a styre-

ne/butylacrylate/acrylate copolymer or a copolymer containing styrene and butadiene.

15. Composition according to any of claims 10 to 14 in which the weight ratio of water soluble polymer (a) to water insoluble polymer (b) is 2 - 50% to 98 - 50% and preferably 3 - 25% to 97 - 75%.

16. Composition according to any of claims 10 to 15 in which the combined amount of water soluble polymer (a) and water insoluble polymer (b) is 2 to 25% by weight and preferably 5 to 20% by weight, based on the weight of the starch.

17. Composition according to any of claims 10 to 16 which includes an additional component selected from Group IV metal salts.

INTERNATIONAL SEARCH REPORT

Inter. nal Application No
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A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 D21H21/16 //D21H17:28,D21H17:34

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 D21H

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,X	WO 97 41186 A (INT PAPER CO) 6 November 1997 see page 3, line 5 - page 5, line 2; examples 1,2	1,2,10, 11
X	DATABASE WPI Section Ch, Week 9333 Derwent Publications Ltd., London, GB; Class A89, AN 93-261339 XP002065166 & JP 05 177 921 A (MITSUBISHI PAPER MILLS LTD) see abstract	1,3,9, 10,12
P,A	WO 97 22754 A (DOW CHEMICAL CO ;FINLAYSON MALCOLM F (US); SPRINGS KENNETH E (US);) 26 June 1997 see the whole document	1,9

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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
18 May 1998	27/05/1998

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Inter nal Application No
PCT/EP 98/00266

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication,where appropriate, of the relevant passages	Relevant to claim No.
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INTERNATIONAL SEARCH REPORT

Information on patent family members

Interr ıal Application No
PCT/EP 98/00266

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